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A model for void-induced back reaction between radiolytic products in NaCl

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Abstract

A kinetic model is formulated for the chemical reaction between radiolytic sodium colloids and gas bubbles, which are brought into contact with each other during the exposure to ionising radiation by the growing voids. The reaction starts with the evaporation of Na atoms into the void due to the localized heat release caused by reactions between chlorine molecules colliding with the colloid surface. It is shown that this exothermic and autocatalytic reaction leads to a sudden temperature increase inside the void, which gives rise to thermoelastic stresses in the surrounding matrix. Tangential stresses might exceed the threshold stress required for localized cleavage of the matrix resulting in crack formation and mechanical instability of NaCl under high dose irradiation. © 2002 Published by Elsevier Science B.V.

Keywords: NaCl radiolysis; Radiation-induced fracture

1. Introduction

Rock salt is considered as one of the candidate host rock materials for retrievable storage of high level radioactive waste. Irradiation of NaCl samples generates H and F centres, which are collected together to form chlorine bubbles and sodium colloids [1]. Our experiments [2–4] on different NaCl samples, heavily irradiated with 0.5 MeV electrons up to fluences of 6×10^{18} cm^{-2}, have shown that with increasing irradiation dose, voids are formed followed by explosion-like fracture of the material. We explain this by a back reaction between radiolytic products. Indeed, according to our model of void formation [5,6], fast growing voids bring chlorine bubbles and Na colloids into contact, which results in the instantaneous back reaction between the radiolytic Na and Cl. In our previous paper [7] the kinetics of the exothermic back reaction was considered assuming that after colloid–void collision the colloid instantaneously evaporates into the void. Here we present a more detailed description of the kinetics of back reaction taking into account the initial stages of the Na colloid evaporation into the void. It will be shown that the temperature increase due to the reaction gives rise to thermoelastic stresses in the NaCl matrix.

2. Back reaction model

According to the model in [6], radiation-induced chlorine bubbles are the most finely dispersed

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extended defects in the sample: $R_B < R_C < R_V$ (here subscripts B, C and V refer to bubbles, colloids and voids, respectively). Because of their higher growth rate voids collect chlorine gas by sweeping the bubbles by its moving boundary. The concentration of chlorine molecules, c_{Cl_2}, captured by the void equals to $0.5V_C$, where V_C is the colloid volume fraction [8] (all concentrations are defined in terms of atomic fractions). Further growth of the void results in collision with a Na colloid. This is expected to occur when the radius of the void reaches values equal to the mean distance between colloids $R_V = (3/4\pi N_C)^{1/3}$, where N_C is the colloid density. When the void collides with a Na colloid, chlorine molecules start hitting the colloid surface and react with Na atoms. The reaction between Cl_2 and Na is a fast exothermic reaction, with null threshold energy [9]. It takes place practically during all collisions of the appropriate particles and proceeds in two stages:

$$\begin{aligned} &Na + Cl_2 \rightarrow NaCl + Cl + q_{NaCl} \\ &Na + Cl \rightarrow NaCl + q_{NaCl} \end{aligned} \quad (1)$$

The first stage of the reaction is envisaged as the transfer of a valence electron of the alkali metal atom to the halogen molecule. The metal atom, in effect, uses its valence electron as a "harpoon" in order to pull in the halogen molecule. The largest separation at which the charge transfer can take place from Na to Cl is estimated as [9]

$$R_{trap} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{p_{Na} - \phi_{Cl}} = 0.95 \text{ nm}, \quad (2)$$

where e is the electron charge. [1] Due to the formation of one NaCl molecule the energy q_{NaCl} is released locally at the colloid surface. The amount of energy is large enough to cause evaporation of several Na atoms, since $q_{NaCl}/(q_f + q_e) = 4.08$ (Fig. 1). We assume that each reaction at the colloid surface leads to the injection into the void of one chlorine atom and of $m = 3$ atoms of sodium. Let us estimate the reaction rate due to thermal fluxes of chlorine atoms and molecules at the colloid surface. The number of reaction events at the colloid surface per second equals the total flux of corresponding particles at the colloid surface,

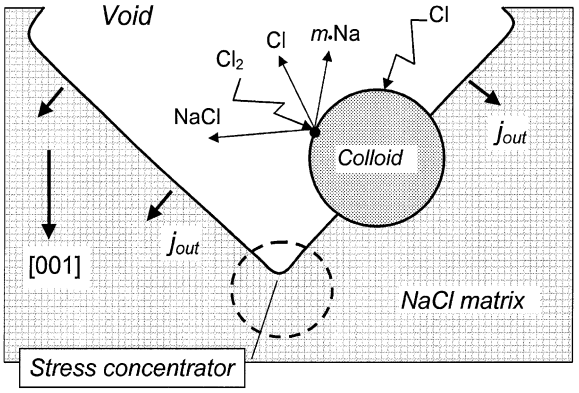

Fig. 1. Illustration of colloid evaporation into the void. mxNa atoms evaporated from the colloid react with Cl and Cl_2. The released energy warms up the gas and increases the chlorine mobility. Hence, the flux of chlorine to the colloid surface increases, i.e. the back reaction has a positive feedback. Cleavage of the matrix is expected to occur along [0 0 1] directions at the void edges, which are the stress concentrators.

$$J_i = \zeta 2\pi R_C^2 \frac{c_i}{\omega}\langle v_i\rangle, \quad i = Cl_2, Cl, \quad (3)$$

where ζ is the fraction of the colloid hemisphere exposed to the gas in the void, $\langle v_i\rangle = (8k_BT/\pi m_i)^{1/2}$ is the average thermal velocity (m_i is the mass). Because of reaction-induced sputtering, the colloid shrinks with time. Initially, on the average, the total number of Na atoms in the colloid equals the number of chlorine atoms captured by the void. Since the total number of Na atoms is conserved, the colloid radius can be related to the void radius and concentrations, c_{Na} and c_{NaCl}, of Na and NaCl in the gas phase,

$$\begin{aligned} R_C &= R_V(2c_{Cl_2}|_{t=0} - c_{Na} - c_{NaCl})^{1/3} \\ &= R_V(V_C - c_{Na} - c_{NaCl})^{1/3}. \end{aligned} \quad (4)$$

To describe the accumulation and dissipation of heat we use a phenomenological model of diffusion-controlled bimolecular reactions with temperature dependent reaction rate constants. The concentrations of particles in the gas phase change with time according to the following equations:

[1] The meaning of parameters is explained in Table 1.

$$\begin{aligned}
\dot{c}_{\mathrm{Na}} &= -\alpha_{\mathrm{NaCl_2}} c_{\mathrm{Na}} c_{\mathrm{Cl_2}} - \alpha_{\mathrm{NaCl}} c_{\mathrm{Na}} c_{\mathrm{Cl}} + m(j_{\mathrm{Cl_2}} + j_{\mathrm{Cl}}),\\
\dot{c}_{\mathrm{Cl_2}} &= -\alpha_{\mathrm{NaCl_2}} c_{\mathrm{Na}} c_{\mathrm{Cl_2}} - j_{\mathrm{Cl_2}},\\
\dot{c}_{\mathrm{Cl}} &= \alpha_{\mathrm{NaCl_2}} c_{\mathrm{Na}} c_{\mathrm{Cl_2}} - \alpha_{\mathrm{NaCl}} c_{\mathrm{Na}} c_{\mathrm{Cl}} + j_{\mathrm{Cl_2}} - j_{\mathrm{Cl}},\\
\dot{c}_{\mathrm{NaCl}} &= \alpha_{\mathrm{NaCl_2}} c_{\mathrm{Na}} c_{\mathrm{Cl_2}} + \alpha_{\mathrm{NaCl}} c_{\mathrm{Na}} c_{\mathrm{Cl}} + j_{\mathrm{Cl_2}} + j_{\mathrm{Cl}}.
\end{aligned} \tag{5}$$

Differently from the equations in [7], these equations contain terms describing contributions to the rates of change due to reactions at the colloid surface, which are induced by thermal fluxes of chlorine atoms and molecules (Eqs. (3) and (4)),

$$j_i = \frac{3\omega}{4\pi R_{\mathrm{V}}^3} J_i = \zeta \frac{3}{2R_{\mathrm{V}}} c_i \langle v_i \rangle \left(V_{\mathrm{C}} - c_{\mathrm{Na}} - c_{\mathrm{NaCl}}\right)^{2/3}, \quad i = \mathrm{Cl_2}, \mathrm{Cl}. \tag{6}$$

The diffusion-controlled reaction rates α_{ij} are given by

$$\alpha_{ij} = \frac{4\pi r_{ij}}{\omega}\left(D_i + D_j\right), \quad D_i = \frac{1}{3}\lambda_i \langle v_i \rangle, \quad i, j = \mathrm{Na}, \mathrm{Cl}, \mathrm{Cl_2}, \mathrm{NaCl}, \tag{7}$$

where D_i and D_j are the diffusion coefficients; r_{ij} is the distance of closest approach between the participating atoms/molecules i and j, which is greater than the sum of the radii $r_i + r_j$, but less than R_{trap} (see Eq. (2)). The collision free path λ_i in the gas mixture is defined as

$$\lambda_i = \omega \left(\sum_j c_j \pi \left(r_i + r_j\right)^2 \sqrt{1 + m_i/m_j} \right)^{-1}. \tag{8}$$

Using the heat balance condition equation describing the time evolution of the temperature inside the void is

$$\begin{aligned}
\frac{\mathrm{d}T}{\mathrm{d}t} &= \frac{[q_{\mathrm{NaCl}} + (2C_1 - C_2)T]\alpha_{\mathrm{NaCl}} c_{\mathrm{Na}} c_{\mathrm{Cl}} + q_{\mathrm{NaCl}} \alpha_{\mathrm{NaCl_2}} c_{\mathrm{Na}} c_{\mathrm{Cl_2}}}{C_1(c_{\mathrm{Na}} + c_{\mathrm{Cl}}) + C_2(c_{\mathrm{NaCl}} + c_{\mathrm{Cl_2}})}\\
&\quad - \frac{3\omega}{R_{\mathrm{V}}} \frac{j_{\mathrm{out}}}{C_1(c_{\mathrm{Na}} + c_{\mathrm{Cl}}) + C_2(c_{\mathrm{NaCl}} + c_{\mathrm{Cl_2}})}\\
&\quad - T \frac{C_1(m+1)j_{\mathrm{Cl_2}} + C_2(m-1)j_{\mathrm{Cl}}}{C_1(c_{\mathrm{Na}} + c_{\mathrm{Cl}}) + C_2(c_{\mathrm{NaCl}} + c_{\mathrm{Cl_2}})}.
\end{aligned} \tag{9}$$

To find the heat flux from the void to the matrix j_{out} the temperature $T(t)$ inside the void is assumed to be uniform and equal to its value at the void boundary. Then j_{out} is given by [8]

$$j_{\mathrm{out}} = \frac{k}{\sqrt{\pi a}} \frac{\mathrm{d}}{\mathrm{d}t} \int_0^t \frac{T(\tau) - T_0}{\sqrt{t - \tau}} \mathrm{d}\tau + \frac{k}{R_{\mathrm{V}}}\left(T(t) - T_0\right), \tag{10}$$

where $a = k/C_m d_m$ is the thermal diffusivity.

Eqs. (5), (9) and (10) form a complete set of integro-differential equations with the initial conditions

$$\begin{aligned}
&T(0) = T_0, \quad c_{\mathrm{Cl_2}}(0) = V_{\mathrm{C}}/2,\\
&c_{\mathrm{Na}}(0) = c_{\mathrm{Cl}}(0) = c_{\mathrm{NaCl}}(0) = 0.
\end{aligned} \tag{11}$$

Once the set is solved, the temperature distribution $\Theta(r,t) + T_0$ around the void can be found,

$$\Theta(r,t) = \frac{R_{\mathrm{V}}(r - R_{\mathrm{V}})}{2r\sqrt{\pi a}} \int_0^t \frac{T(\tau) - T_0}{(t - \tau)^{2/3}} \times \exp\left(- \frac{(r - R_{\mathrm{V}})^2}{4a(t - \tau)} \right) \mathrm{d}\tau. \tag{12}$$

A non-uniform temperature distribution produces thermoelastic stresses in an elastic medium [10]. In a spherical system of coordinates the tangential stresses around the void $\sigma_{\theta\theta}$ and $\sigma_{\varphi\varphi}$ are greater than radial stresses,

$$\begin{aligned}
\sigma_{\theta\theta} &= \sigma_{\varphi\varphi}\\
&= \varepsilon \frac{E}{1 - \nu} \left(\frac{1}{r^3} \int_{R_{\mathrm{V}}}^r \Theta(\rho, t) \rho^2 \mathrm{d}\rho - \Theta(r,t) \right)\\
&\quad + \frac{R_{\mathrm{V}}^3}{2r^3} \frac{k_{\mathrm{B}} T}{\omega} \sum_i c_i,
\end{aligned} \tag{13}$$

where the last term is due to the gas pressure inside the void. To find the criterion for the matrix stability against cracking the thermoelastic stresses should be compared with the threshold stress required for cleavage of the matrix [11]

$$\sigma_{\mathrm{fr}}(R_{\mathrm{V}}) = 0.5\sigma_{\mathrm{Gr}} = 0.5\sqrt{\frac{E\gamma_{\mathrm{V}}}{\pi(1 - \nu^2)R_{\mathrm{V}}}}, \tag{14}$$

where σ_{Gr} is the stress corresponding to the Griffith crack of the length $2R_{\mathrm{V}}$. Note that real voids are not spherical [2–4], so the actual stresses can be higher than estimated by Eq. (13).

3. Results of calculations

The set of Eqs. (5), (9)–(11) was solved numerically using material parameters listed in Table 1. The algorithm of the solution is described in [7]. It was found that the time dependence of the back reaction is controlled by the evaporation process and heat conduction into the matrix. Reaction in the void volume is much faster than these two processes. Below we present the typical results of calculations. Fig. 2(a) shows time dependence of concentrations of reagents and reaction products. The concentration of Na atoms in the gas phase is small because the evaporated atoms react very quickly with chlorine molecules and atoms in the void. Fig. 2(b) depicts the build up and decrease of the temperature at the void surface during the back reaction. The temperature increase results in the appearance of large thermoelastic stresses around the void. The time dependence of the tangential stresses at the void surface is shown in Fig. 2(c) along with the threshold value $\sigma_{\rm fr}$ for the stress to cause cleavage. Assuming that the crack propagates with the sound velocity, we estimate that the crack may propagate over a distance of about 10^3 nm during the time interval when the local stresses exceed the threshold stress. Fig. 3 shows the dependence of the maximum tangential stress at the void surface, $\max(\sigma_{\theta\theta}(r,t))$ on the colloid parameters. It is seen that the matrix is stable with respect to crack formation ($\max(\sigma_{\theta\theta}(r,t)) < \sigma_{\rm fr}$) at low volume fractions and/or high colloid densities. The maximum stress increases approximately linearly with the colloid volume fraction. Fig. 4 summarizes the results of this work in the form of a stability diagram for irradiated NaCl samples. This diagram correlates with experimental data – NaCl samples doped with Li and Br exhibit enhanced mechanical stability, whereas

Table 1
Material parameters used in calculations

Matrix temperature, T_0, K	400
Multiplication coefficient, m	3
Fraction of colloid hemisphere exposed to Cl gas, ζ	1
Ionization potential of Na, $p_{\rm Na}$, eV	5.138
Electron affinity of Cl, $\phi_{\rm Cl}$, eV	3.617
Heat of formation of NaCl-molecule, $q_{\rm NaCl}$, eV	4.253
Heat of fusion of Na, $q_{\rm f}$, eV atom^{-1}	0.027
Heat of vaporization of Na, $q_{\rm e}$, eV atom^{-1}	1.0158
Density of NaCl, d_m, kg m^{-3}	2165
Atomic volume of NaCl, ω, nm^3	4.5×10^{-2}
Young's modulus of NaCl, E, Gpa	39.98
Poisson ratio, v	0.252
Thermal conductivity of NaCl, k, W m^{-1} K^{-1}	1.15
Specific heat capacity of NaCl, C_m, J kg^{-1} K^{-1}	854
Specific heat capacity at a constant volume of mono and di-atomic gases, C_1 and C_2, per particle	$1.5k_{\rm B}$, $2.5k_{\rm B}$
Coefficient of thermal expansion, ε, K^{-1}	4.4×10^{-5}
Sound velocity in NaCl, $V_{\rm sound}$, m s^{-1}	4.78×10^3
Surface energy of NaCl, $\gamma_{\rm V}$, J m^{-2}	0.384

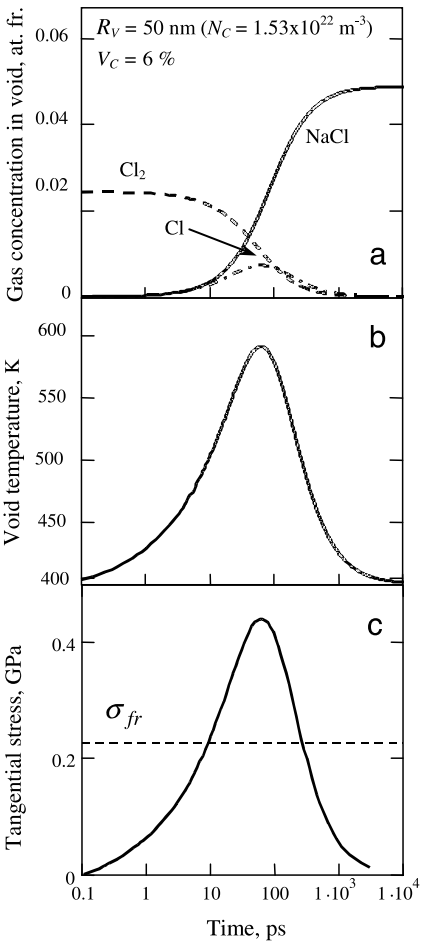

Fig. 2. Time dependence of (a) the gas concentrations in the void, (b) the temperature increase and (c) the absolute value of the tangential stress at the void surface. Note the logarithmic time scale.

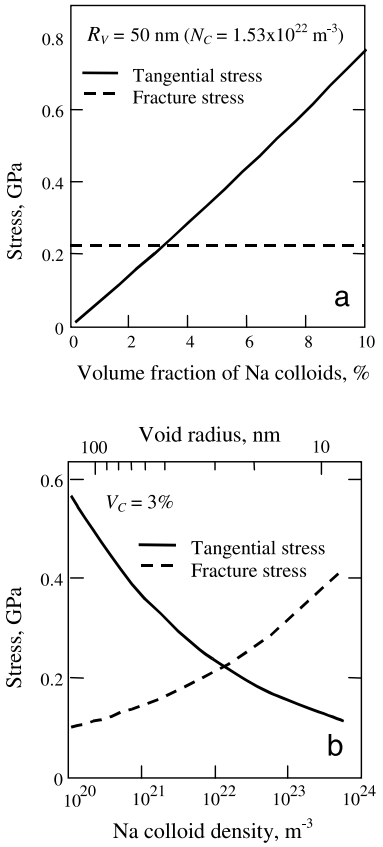

Fig. 3. Dependence of the tangential stress at the void surface on (a) the colloid volume fraction and (b) the colloid density.

NaCl samples with K and natural rock salt are characterized by an early start and a rapid progress of the void-crack transition, resulting in unconstrained propagation of cracks and subsequent explosive fracture of the material.

4. Conclusions

- Growing voids in NaCl subjected to ionizing irradiation absorb radiolytic chlorine and sodium providing a place for instantaneous back reactions accompanied by rapid heat release.
- The maximum thermoelastic tangential stresses induced by the back reaction at the void surface increase almost linearly with colloid volume fraction and might easily exceed the threshold pressure required for crack propagation from the void along one of the (1 0 0) cleavage planes of the matrix.
- The diagram of mechanical stability agrees with experimental data and shows that no fracture is expected in NaCl materials containing a low volume fraction of voids and/or a high colloid density.

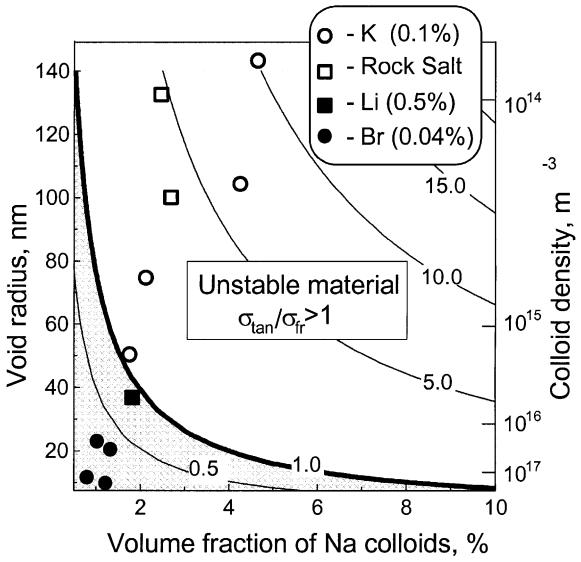

Fig. 4. Stability diagram of the of NaCl against fracture, including the experimental data points obtained for several doped NaCl crystals and natural rock salt. The labeled curves are the contour lines of the ratio of tangential stress at the void surface relative to the fracture stress, $\max(\sigma_{\theta\theta}(r,t))/\sigma_{\mathrm{fr}}(R_V)$. The shadowed region indicates stable material.

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